POSTFLOOD OCCURENCE OF SELECTED AGRICULTURAL CHEMICALS AND VOLATILE ORGANIC COMPOUNDS IN NEAR-SURFACE UNCONSOLIDATED AQUIFERS

IN THE UPPER MISSISSIPPI RIVER BASIN

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U.S. GEOLOGICAL SURVEY CIRCULAR 1120-G

Front cover—A scene from Minnesota shows the problems caused by the 1993 floods (Bernard Volker, Herman, Minnesota).

Back cover—View of Spirit of St. Louis Airport, Chesterfield, Mo. (Srenco Photography, St. Louis, Mo.)

Field Hydrologist making streamflow measurements (U.S. Geological Survey)

POSTFLOOD OCCURRENCE OF SELECTED AGRICULTURAL CHEMICALS AND VOLATILE ORGANIC COMPOUNDS IN NEAR-SURFACE UNCONSOLIDATED AQUIFERS IN THE UPPER MISSISSIPPI RIVER BASIN, 1993

By Dana W. Kolpin and E. Michael Thurman

Floods in the Upper Mississippi River Basin, 1993

U.S. GEOLOGICAL SURVEY CIRCULAR 1120-G

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FOREWORD

During spring and summer 1993, record flooding inundated much of the upper Mississippi River Basin. The magnitude of the damages—in terms of property, disrupted business, and personal trauma—was unmatched by any other flood disaster in United States history. Property damage alone is expected to exceed $10 billion. Damaged highways and submerged roads disrupted overland transportation throughout the flooded region. The Mississippi and the Missouri Rivers were closed to navigation before, during, and after the flooding. Millions of acres of productive farmland remained under water for weeks during the growing season. Rills and gullies in many tilled fields are the result of the severe erosion that occurred throughout the Midwestern United States farmbelt. The hydrologic effects of extended rainfall throughout the upper Midwestern United States were severe and widespread. The banks and channels of many rivers were severely eroded, and sediment was deposited over large areas of the basin's flood plain. Record flows submerged many areas that had not been affected by previous floods. Industrial and agricultural areas were inundated, which caused concern about the transport and fate of industrial chemicals, sewage effluent, and agricultural chemicals in the floodwaters. The extent and duration of the flooding caused numerous levees to fail. One failed levee on the Raccoon River in Des Moines, Iowa, led to flooding of the city's water treatment plant. As a result, the city was without drinking water for 19 days.

As the Nation's principal water-science agency, the U.S. Geological Survey (USGS) is in a unique position to provide an immediate assessment of some of the hydrological effects of the 1993 flood. The USGS maintains a hydrologic data network and conducts extensive water-resources investigations nationwide. Long-term data from this network and information on local and regional hydrology provide the basis for identifying and documenting the effects of the flooding. During the flood, the USGS provided continuous streamflow and related information to the National Weather Service (NWS), the U.S. Army Corps of Engineers, the Federal Emergency Management Agency (FEMA), and many State and local agencies as part of its role to provide basic information on the Nation's surface- and ground-water resources at thousands of locations across the United States. The NWS has used the data in forecasting floods and issuing flood warnings. The data have been used by the Corps of Engineers to operate water diversions, dams, locks, and levees. The FEMA and many State and local emergency management agencies have used USGS hydrologic data and NWS forecasts as part of the basis of their local flood-response activities. In addition, USGS hydrologists are conducting a series of investigations to document the effects of the flooding and to improve understanding of the related processes. The major initial findings from these studies will be reported in this Circular series as results become available.

U.S. Geological Survey Circular 1120, *Floods in the Upper Mississippi River Basin, 1993*, consists of individually published chapters that will document the effects of the 1993 flooding. The series includes data and findings on the magnitude and frequency of peak discharges; precipitation; water-quality characteristics, including nutrients and man-made contaminants; transport of sediment; assessment of sediment deposited on flood plains; effects of inundation on ground-water quality; flood-discharge volume; effects of reservoir storage on flood peaks; stream-channel scour at selected bridges; extent of flood-plain inundation; and documentation of geomorphologic changes.

Gordon P. Eaton

Director
January 11, 1995

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter
	Area	
acre	0.4047	hectares

Milligram per liter (mg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (milligrams) of solute per unit volume (liter) of water.
Microgram per liter (µg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (micrograms) of solute per unit volume (liter) of water.

Postflood Occurrence of Selected Agricultural Chemicals and Volatile Organic Compounds in Near-Surface Unconsolidated Aquifers in the Upper Mississippi River Basin, 1993

By Dana W. Kolpin *and* E. Michael Thurman

Abstract

The historic stream flooding and intense rainfall across the upper Mississippi River Basin during summer 1993 had an immediate effect on near-surface unconsolidated aquifers by raising the water levels closer to the land surface. The objective of this study was to determine if this flooding also had immediate effects on ground-water quality. Water samples were collected during September and October 1993 from 110 wells completed in near-surface unconsolidated aquifers and were analyzed for herbicides, herbicide metabolites, inorganic nutrients, and volatile organic compounds. The results of these samples were compared with those obtained during summer 1991 or 1992. The difference was not statistically significant in the frequency of herbicide detection, total herbicide concentration, nitrate concentration, or the frequency of volatile organic compound detection between water samples collected in 1991 and 1992 and those collected in 1993 when all 110 wells were considered collectively. However, water samples from the Missouri River alluvial aquifer had a fourfold increase in the frequency of herbicide detection. There also appears to be a relation between increases in total herbicide concentration and the occurrence of stream flooding near a well. Water samples from wells that had at least a 20-percent increase in dissolved-oxygen concentration had the greatest frequency of substantial changes in total herbicide concentration and substantial increases in nitrate concentration. Increased dissolved-oxygen concentration could indicate areas where recharge has increased as a result of extensive stream flooding and intense rainfall. An inverse relation was determined between well depth and changes (increase or decrease) in total herbicide concentration. Water in shallow wells more quickly reflect changes in water quality in response to changes in recharge. Significantly more urban residential and industrial land use was within a 30-meter radius of the well for wells in which volatile organic compounds were detected. Because water moves more slowly along ground-water flow paths compared with surface-water runoff, additional information is required to determine long-term effects of the 1993 flood on ground-water quality.

INTRODUCTION

Flooding was severe across large parts of the upper Mississippi River Basin during summer 1993 (fig. 1). This flooding was unprecedented in terms of its extent, long duration, and extensive damage. At 45 U.S. Geological Survey (USGS) streamflow-gaging stations in 8 Midwestern States, peak discharges exceeded 100-year recurrence intervals (Parrett and others, 1993). At 41 USGS streamflow-gaging stations, the peak discharge was greater than the previous maximum discharge. This record flooding during summer 1993 was facilitated by a wetter-than-normal spring that kept much of the soils in the upper Midwest saturated and a persistent weather pattern that created intense rainfall from June through August. Rainfall during July 1993 was more than 150 percent of normal (1961–90) over much of the upper Mid-

Figure 1. An example of damage caused when the Mississippi River breached a levee near the southern tip of Illinois.

west and more than 400 percent of the normal in several areas (Hillaker, 1993; Wahl and others, 1993).

The 1993 flood also affected the quality of surface waters in the upper Mississippi River Basin. Data collected from the Mississippi River and its tributaries during the flood showed that the large volumes of water did not have the anticipated dilutional effect on the concentrations of agricultural chemicals that were being transported in the river, but simply flushed increased amounts into the river systems (Goolsby and others, 1993). The concentrations of agricultural chemicals in 1993 were similar to those measured at much lower flows during 1991 and 1992, but the corresponding daily chemical loads that were being transported were substantially larger. The total atrazine load transported to the Gulf of Mexico from April through August 1993 was about 80 percent higher than that for the same period in 1991 and about 235 percent higher than that in 1992 (Goolsby and others, 1993).

Ground water is the major source of drinking water in the upper Midwest, and conventional water-treatment practices do not remove most agricultural chemicals. The large increases in the load of agricultural chemicals that were being transported in surface waters in the upper Mississippi River Basin from the 1993 flood raised the concern that transport of these chemicals to ground water, particularly alluvial aquifers, also could be increasing. Possible modes of chemical transport to ground water from flooding include reversed hydraulic gradients due to prolonged high river stages (fig. 2), infiltration of water from overbank flooding (fig. 3), and direct flow down the well casing through inundation of a well (fig. 4).

The 1993 flood increased ground-water recharge and caused an immediate increase in water levels in unconsolidated aquifers. For example, the increase in water level in a well completed in the Mississippi River alluvium in eastern Iowa, is shown in figure 5. About 40 percent of the USGS water-level monitoring wells completed in unconsolidated aquifers in Iowa had the highest water level for their period of record (D. Sneck-Fahrer, U.S. Geological Survey, oral commun., 1994).

Purpose and Scope

The purpose of this study was to determine whether the 1993 flood affected the water quality of near-surface aquifers in the upper Mississippi River Basin. This report presents and summarizes information on the concentrations of agricultural chemicals and volatile organic compounds in water samples from near-

Figure 4. An inundated municipal well along the Cedar River in eastern Iowa.

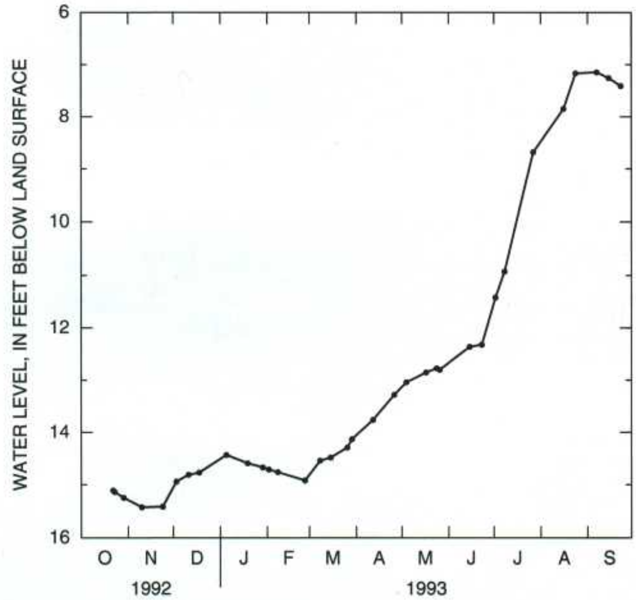

Figure 5. Water level during the 1993 water year for a well completed in the Mississippi River alluvium in eastern Iowa.

surface unconsolidated aquifers in the upper Mississippi River Basin collected during September and October 1993, which was shortly after the worst of the flooding.

Ground water moves slowly compared with surface water. The rate of ground-water movement can vary greatly depending on the materials through which the water passes, the hydraulic conductivity of the unsaturated zone, and the distance from the land surface to the saturated zone. Consequently, additional information is required to determine long-term effects of the 1993 flood on the water quality of near-surface aquifers. For example, changes in the nitrate concentrations of ground water lagged behind changes in the amounts of nitrogen fertilizer usage by about 4 to 19 months (Hall, 1992).

Results of Previous Studies

During 1991, the USGS performed a reconnaissance study to determine the hydrogeologic, seasonal, and geographic distribution of herbicides and nitrate in near-surface aquifers of the midcontinental United States (Kolpin and Burkart, 1991; Burkart and Kolpin, 1993; Kolpin, Burkart, and Thurman, 1993, 1994). Near-surface aquifers were defined as having the top of the aquifer material about 15 m below land surface. A statistical design was used to select 303 wells from which water samples were collected in March or April (preplanting) and July or August (postplanting) 1991. However, seven of these wells could only be sampled once during the 1991 study and 10 water samples could not be analyzed because of lost or broken bottles. Samples were analyzed for 11 herbicides, 2 triazine herbicide metabolites, and 4 inorganic nutrients.

Herbicides or triazine metabolites were detected in about 24 percent of the 589 samples collected for analysis during 1991. Results of this study showed that water from unconsolidated aquifers is more likely to contain herbicides than water from bedrock aquifers (frequency of detection 34 percent compared with 18 percent). Recharge rates generally are faster and recharge sources are in closer proximity to the unconsolidated aquifers than to the bedrock aquifers because of such differences as aquifer geometry and the likelihood of confining conditions (Kolpin and others, 1994). Ground-water samples from wells located within 30 m of a stream had more than twice the frequency of herbicide detection than of wells with no streams nearby (48 percent compared with 22 percent). Because almost all sampled wells within 30 m of a stream were completed in alluvial aquifers, this difference in frequency of herbicide detection could be caused by a hydraulic connection between aquifers and streams. Frequencies of detection and concentrations of herbicides are much larger in streams than in aquifers of the midcontinent (Thurman and others, 1992; Goolsby and Battaglin, 1993). Therefore, recharge to an aquifer by a stream could be a source of herbicide contamination to the aquifer (Squillace and others, 1993).

During 1992, the USGS conducted a follow-up study to investigate why herbicides were not detected in greater than 70 percent of the samples from near-surface aquifers sampled in 1991. By using a stratified-random procedure, 101 wells were selected from the 1991 study network and were resampled once during July or August 1992. The same 13 herbicide compounds and 4 inorganic nutrients were analyzed as in the 1991 study, as well as an additional 45 herbicides, insecticides, and metabolites. A subset of these 101 wells also was sampled for 63 volatile organic compounds.

A pesticide or pesticide metabolite was detected in ground water from about 62 percent of the 101 wells sampled (Kolpin, Goolsby, and others, 1993). The greater frequency of detection during 1992 was the result of an increased number of pesticides and metabolites analyzed and a more sensitive analytical method that had reporting limits that were about an order of magnitude less than those used in 1991.

Ground water from 117 wells were analyzed for tritium concentrations during either the 1991 or 1992 study. The combination of tritium's short half-life (12.3 years), low rate of natural production, and large inputs caused by nuclear testing makes it a useful tool for determining water that has recharged aquifers since 1953 (Bradbury, 1991). For this study, no pesticide or pesticide metabolite concentrations were determined (at 0.05 μg/L reporting limits) in wells containing "old" water. Because agricultural chemicals, such as atrazine, have been used to enhance crop yields only during the last 40 years, the absence of pesticide detection in wells that contain water recharged before 1953 ("old" water) was expected.

STUDY DESIGN AND METHODS

Because the greatest effect on water quality of near-surface aquifers was expected in the areas with the greatest rainfall and stream flooding, the study region was defined as the area with more than 150 percent of normal rainfall from April 1 to July 31, 1993, (Climate Analysis Center, National Weather Service, written commun., 1993) (fig. 6). Information from the 1991–1992 studies was used to select wells that would have the greatest potential for determining the immediate effects of the 1993 flood on ground-water quality. The initial well selection identified 114 wells from the network that were completed in unconsolidated aquifers that contained "new" (post-1953) water and were located in the high-rainfall region. However, six of these wells could not be sampled as a result of either the well owner declining to participate in the study or continued inundation by flood water; two of these wells were replaced with alternative sampling wells known to be in an area with flood problems during 1993. One of these alternative wells happen to reside outside the study region. The 110 wells selected for study were sampled during September or October 1993.

Data-Collection Methods

Methods to collect and process the water samples were the same as those used for the 1991 and 1992 studies (Kolpin and Burkart, 1991; Kolpin, Goolsby, and others, 1993). All samples were collected by USGS personnel with equipment constructed of materials, such as glass and stainless steel, that would not leach or adsorb organic compounds. Decontamination procedures were implemented to prevent cross-contamination of water between wells and samples. Wells were purged before sampling until pH, water temperature, and specific conductance stabilized. Where possible, water levels were measured before purging. However, water levels could be measured in only 25 of the 110 wells sampled. Well owners were interviewed to determine how the flooding and intense rainfall may have affected the area that surrounds the sampled wells.

The concentrations of 11 herbicides (alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, propazine, prometryn, simazine, and terbutryn) and 2 triazine herbicide metabolites [deethylatrazine (DEA), deisopropylatrazine (DIA)] were determined by extraction on disposable C-18 solid-phase extraction cartridges followed by gas chromatography/mass spectrometry (GC/MS) (Thurman and others, 1990; Meyer and others, 1993). The analytical reporting limit for these herbicides and her-